

StatMech seminar 3: Theoretical part

Volodya Sergiievskyi

November 2, 2009

1

1.1 What is a conditional probability?

Let we have events $A, B \in \Omega$. Conditional probability $P(A|B)$ is the probability of event a, given the event B. It is defined by:

$$P(A|B) = \frac{P(AB)}{P(B)} \quad (1)$$

where

$P(B)$ is the probability of event B

$P(AB)$ is the probability of event (A and B)

1.2 What is a conditional density?

Conditional density is the mean number of particles per unit of volume at the point \mathbf{r}_1 , given a particle at the point \mathbf{r}_2 . It can be found from the two-particles density function:

$$\rho(\mathbf{r}_1|\mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} \quad (2)$$

where

$\rho(\mathbf{r}_1)$ is the one-particle density at the point \mathbf{r}_1

$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is two-particle distribution function (6) *Details see below*

1.3 What is a pair distribution function?

Let system has N particles. We will use a notation:

$$\begin{aligned} d\mathbf{r}_i &= (dx_i, dy_i, dz_i) = (x_i; x_i + \Delta x) \times (y_i; y_i + \Delta y) \times (z_i; z_i + \Delta z) \\ d\mathbf{p}_i &= (dp_x^i, dp_y^i, dp_z^i) = (p_x^i; p_x^i + \Delta p_x) \times (p_y^i; p_y^i + \Delta p_y) \times (p_z^i; p_z^i + \Delta p_z) \end{aligned} \quad (3)$$

where $\Delta x, \Delta y, \Delta z, \Delta p_x, \Delta p_y, \Delta p_z$ are infinitesimal.

Let

$$d\omega(\mathbf{r}^N, \mathbf{p}^N) = D_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \quad (4)$$

is the probability to find

particle 1 in the infinitesimal valume $d\mathbf{r}_1$ AND

particle 2 in the infinitesimal valume $d\mathbf{r}_2$ AND

...

particle N in the infinitesimal valume $d\mathbf{r}_N$

where

$\mathbf{r}^N = \mathbf{r}_1, \dots, \mathbf{r}_N$ are coordinates of particles
 $\mathbf{p}^N = \mathbf{p}_1, \dots, \mathbf{p}_N$ are momenta of particles

Let's define a n particles distribution function as the mean number of particles per volume at the coordinates \mathbf{r}^n , not considering their momenta. This function can be found from the probability to find labeled particles by integration over momenta and $(N-n)$ coordinates and summation over all possible permutations of particle coordinated (there are $\frac{N!}{(N-n)!}$ of them).

$$\rho^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} \int D_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{(N-n)} \quad (5)$$

where

D_N is the probability density in phase space (see (4))

$\mathbf{r}^n = \mathbf{r}_1, \dots, \mathbf{r}_n$

$d\mathbf{r}^{(N-n)} = d\mathbf{r}_{n+1} \dots d\mathbf{r}_N$

In the case $n = 2$ we have pair distribution function:

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int D_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{(N-2)} \quad (6)$$

The definition (6) can be rewritten as:

$$\rho^{(2)}(\mathbf{r}', \mathbf{r}'') = N(N-1) \int D_N(\mathbf{r}^N, \mathbf{p}^N) \delta(\mathbf{r}' - \mathbf{r}_1) \delta(\mathbf{r}'' - \mathbf{r}_2) d\mathbf{r}^{(N)} \quad (7)$$

That means, that the definition of pair distribution function can be rewritten in the terms of ensemble averaging:

$$\rho^{(2)}(\mathbf{r}', \mathbf{r}'') = N(N-1) \langle \delta(\mathbf{r}' - \mathbf{r}_1) \delta(\mathbf{r}'' - \mathbf{r}_2) \rangle = \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_j) \right\rangle \quad (8)$$

1.4 and how it is related with conditional probability?

Pair particle correlation function is the deviation of density of one particle at position \mathbf{r}_1 given the another particle at position \mathbf{r}_2 .

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_1 | \mathbf{r}_2)}{\rho(\mathbf{r}_1)} \quad (9)$$

where $\rho(\mathbf{r}_1 | \mathbf{r}_2)$ is conditional density (2).

Using we formula (2) we found the equivalent definition of pair distribution function:

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)} \quad (10)$$

where $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is pair distribution function (6).

From that definition one can see, that pair correlation function is symmetric:

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_1 | \mathbf{r}_2)}{\rho(\mathbf{r}_1)} = \frac{\rho(\mathbf{r}_2 | \mathbf{r}_1)}{\rho(\mathbf{r}_2)} = g(\mathbf{r}_2, \mathbf{r}_1) \quad (11)$$

Form the definition (9) we may find the relation between the conditional probability (2) and pair distribution function (6)

$$\rho(\mathbf{r}_1 | \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_1) \quad (12)$$

1.5 How the pair distribution function is related with the radial distribution function (RDF)?

isotropic case If we have an isotropic case, the pair correlation function (11) will not change while the shifting the coordinates:

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1 - \mathbf{r}, \mathbf{r}_2 - \mathbf{r}) \quad (13)$$

In that case we may consider one of the particles to be at the origin, and denote:

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) \equiv g(\mathbf{r}) \quad (14)$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$

If the space is rotationally isotropic, then $g(\mathbf{r})$ is only a function of distance between particles:

$$g(\mathbf{r}) \equiv g(r) \quad (15)$$

where $r = |\mathbf{r}|$

The function $g(r)$ is called *Radial Distribution Function (RDF)* for the isotropic case

As well, in isotropic case the one-particle density is the same over the all volume:

$$\rho(\mathbf{r}) = \frac{N}{V} = \rho \quad (16)$$

Then, using the definition of density correlation function (11) and relations (15),(14) we obtain relation between the isotropic RDF function and pair distribution function:

$$\rho^{(2)}(r) \equiv \rho(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) = \rho^2 g(r) \quad (17)$$

where $r = |\mathbf{r}_2 - \mathbf{r}_1|$

Using the definition of conditional density (2):

$$\rho(r|\mathbf{r}_2) \equiv \rho(\mathbf{r}_1|\mathbf{r}_2) = \rho g(r) \quad (18)$$

where $r = |\mathbf{r}_2 - \mathbf{r}_1|$

This is the density at the distance r from the particle at coordinates \mathbf{r}_2

non-isotropic case In the non-isotropic case, we can define the equality, similar to (18)). The only thing we need - to take average of conditional density over all points which are on distance r from the particle in point \mathbf{r}_2 :

$$\rho(r|\mathbf{r}_2) \equiv \frac{1}{4\pi r^2} \int_{S(r)} \rho(\mathbf{r}_1|\mathbf{r}_2) d\mathbf{r}_1 \equiv \bar{\rho} g(r) \quad (19)$$

where

$S(r)$ is a sphere with center in \mathbf{r}_2 and radius r

$4\pi r^2$ is the area of sphere $S(r)$

$\bar{\rho}$ is the mean density:

$$\bar{\rho} = \frac{\int \rho(\mathbf{r}) d\mathbf{r}}{\int d\mathbf{r}} = \frac{N}{V} \quad (20)$$

Then, RDF around the point \mathbf{r}_2 might be defined as:

$$g(r|\mathbf{r}_2) = \frac{1}{4\pi \bar{\rho} r^2} \int_{S(r)} \rho(\mathbf{r}_1|\mathbf{r}_2) d\mathbf{r}_1 \quad (21)$$

Using the relation (2) we may as well rewrite:

$$g(r|\mathbf{r}_2) = \frac{1}{4\pi\bar{\rho}\rho(\mathbf{r}_2)r^2} \int_{S(r)} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 \quad (22)$$

if we consider coordinates of some particle as the origin, we have

$$\rho(\mathbf{r}_2) = \delta(\mathbf{r}_2) \quad (23)$$

and definition of RDF function might be rewritten:

$$g(r) \equiv g(r|\mathbf{0}) = \frac{1}{4\pi\bar{\rho}r^2} \int_{S(r)} \rho^{(2)}(\mathbf{r}_1, \mathbf{0}) d\mathbf{r}_1 \quad (24)$$

2 Virial equation

2.1 Lema: Averaging pairwise function

Let we have function

$$F(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N f(\mathbf{r}_i, \mathbf{r}_j) \quad (25)$$

Ensemble average of this function is:

$$\langle F \rangle = \sum_{i=1}^N \sum_{j=i+1}^N \langle f(\mathbf{r}_i, \mathbf{r}_j) \rangle = \frac{N(N-1)}{2} \langle f(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (26)$$

We may rewrite it as:

$$\langle F \rangle = \frac{1}{2} \int f(\mathbf{r}_1, \mathbf{r}_2) \left(N(N-1) \int D_N(\mathbf{r}^N) d\mathbf{r}^{(N-2)} \right) d\mathbf{r}_1 d\mathbf{r}_2 \quad (27)$$

where

$D_N(r^N)$ is probability density of N particle distribution (4)
 $d\mathbf{r}^{(N-2)} = d\mathbf{r}_3 \dots d\mathbf{r}_N$

Considering definition of pair distribution function (6), we found:

$$\langle F \rangle = \frac{1}{2} \int f(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (28)$$

2.2

As was discussed previously, pressure can be found by the formula:

$$P = - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_{N,T} \quad (29)$$

where \mathcal{F} is Helmholtz Free Energy:

$$\mathcal{F} = -k_B T \ln \frac{1}{N! \Lambda^{3N}} Q_N = k_B T \ln N! \Lambda^{3N} - k_B T \ln Q_N \quad (30)$$

where Q_N is configurational integral

$$Q_N = \int e^{-\frac{1}{k_B T} U_N(\mathbf{r}^N)} d\mathbf{r}^N \quad (31)$$

and $U_N(\mathbf{r}^N)$ is potential energy of a system.

The first summand in (30) ($k_B T \ln N! \Lambda^{3N}$) is independent of volume V , and gives zero after differentiation. Putting to the (29) Free Energy (30) we obtain:

$$P = \frac{k_B T}{Q_N} \left(\frac{\partial Q_N}{\partial V} \right)_{N,T} \quad (32)$$

2.3

Let's introduce new variables r_i^* such, that

$$\mathbf{r}_i = L \mathbf{r}_i^* \quad (33)$$

and

$$\int \mathbf{r}^{*N} d\mathbf{r}^{*N} = 1 \quad (34)$$

In that case we have:

$$V = \int \mathbf{r}_1 = L^3 \int \mathbf{r}_1^* = L^3 \quad (35)$$

Putting it to (32) we obtain:

$$P = \frac{k_B T}{Q_N} \frac{\partial Q}{\partial L} \frac{\partial L}{\partial V} = \frac{k_B T}{Q_N} \frac{\partial Q}{\partial L} \frac{1}{3L^2} \quad (36)$$

2.4

Configurational integral (31) in coordinates (33) becomes:

$$Q_N = L^{3N} \int e^{-\frac{1}{k_B T} U_N(L\mathbf{r}^{*N})} d\mathbf{r}^{*N} \quad (37)$$

Putting it to (36) we obtain

$$\begin{aligned} P &= \frac{k_B T}{3L^2} \frac{1}{L^{3N}} \frac{1}{\int e^{-\frac{1}{k_B T} U_N} d\mathbf{r}^{*N}} \frac{\partial}{\partial L} \left(L^{3N} \int e^{-\frac{1}{k_B T} U_N(L\mathbf{r}^{*N})} d\mathbf{r}^{*N} \right) \\ &= \frac{k_B T}{3L^2} \left(\frac{3N}{L} - \frac{1}{k_B T} \int \left(\frac{e^{-\frac{1}{k_B T} U_N}}{Q_N} \right) \frac{\partial U_N(\mathbf{r}^{*N})}{\partial L} d\mathbf{r}^{*N} \right) \end{aligned} \quad (38)$$

As was said in the previous chapter, the probability to find particles at the coordinates \mathbf{r}^N is:

$$D_N^{(r)} = \frac{e^{-\frac{1}{k_B T} U_N}}{Q_N} \quad (39)$$

And we have:

$$P = \frac{N}{V} k_B T - \frac{1}{L^2} \int D_N^{(r)} \frac{\partial U_N(\mathbf{L}\mathbf{r}^{*N})}{\partial L} d\mathbf{r}^N = \rho k_B T - \frac{1}{L^2} \left\langle \frac{\partial U_N(\mathbf{L}\mathbf{r}^{*N})}{\partial L} \right\rangle \quad (40)$$

2.5 Pairwise potential

Let's consider the case of pairwise potential:

$$U_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N u(r_{ij}) \quad (41)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ It's easy to see, that $r_{ij} = Lr_{ij}^*$, where $r_{ij}^* = |r_i^* - r_j^*|$ And also:

$$\frac{\partial r_{ij}}{\partial L} = \frac{\partial Lr_{ij}^*}{\partial L} = r_{ij}^* = \frac{r_{ij}}{L} \quad (42)$$

The partial derreivative of equality (41):

$$\frac{\partial U_N}{\partial L} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{\partial u(r_{ij})}{\partial r_{ij}} \frac{\partial Lr_{ij}^*}{\partial L} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{\partial u(r_{ij})}{\partial r_{ij}} \frac{r_{ij}}{L} \quad (43)$$

Using the lema (28) we may found ensemble average:

$$\left\langle \frac{\partial U_N(\mathbf{Lr}^{*N})}{\partial L} \right\rangle = \frac{1}{2L} \int \frac{\partial u(r_{12})}{\partial r_{12}} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12} d\mathbf{r}_1 d\mathbf{r}_2 \quad (44)$$

We integrate *twice* over whole volume, however our functions depends only on distance, not on the coordinate by itself. It sould result, that seconond integration will simply produce multiplication by whole volume:

$$\begin{aligned} \left\langle \frac{\partial U_N(\mathbf{Lr}^{*N})}{\partial L} \right\rangle &= \frac{1}{2L} \int \left(\int \frac{\partial u(r_{12})}{\partial r_{12}} \rho^{(2)}(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) r_{12} d(\mathbf{r}_2 - \mathbf{r}_1) \right) d\mathbf{r}_2 \\ &= \frac{V}{2L} \int \frac{\partial u(r_{12})}{\partial r_{12}} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12} d(\mathbf{r}_2 - \mathbf{r}_1) \end{aligned} \quad (45)$$

Using relation (17) we may change interation by volume to the integration of shperes:

$$\left\langle \frac{\partial U_N(\mathbf{r}^N)}{\partial L} \right\rangle = \frac{4\pi\rho^2 V}{2L} \int_0^\infty \frac{\partial u(r_{12})}{\partial r_{12}} r_{12}^3 g(r_{12}) dr_{12} \quad (46)$$

Putting this to the (40) we obtain the final formula:

$$P = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{\partial u(r)}{\partial r} r^3 g(r) dr \quad (47)$$

This is *Virial* equation, which allow us to find the preasure given the RDF.

2.6 Internal Energy

Internal energy is sum of kinetic and potential part:

$$E = \langle K(\mathbf{p}^N) \rangle + \langle U_N(\mathbf{r}^N) \rangle \quad (48)$$

where

$K(\mathbf{p}^N)$ is kinetic

$U_N(\mathbf{r}^N)$ is potential energy

The contribution of kinetic energy with particles with maxwellian distribution is known:

$$\langle K(\mathbf{p}^N) \rangle = \frac{3}{2} N k_B T \quad (49)$$

Let's consider case, then all interactions between particles depends only on distance between them:

$$U_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N u(r_{ij}) \quad (50)$$

where

$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is a distance between particles

$u(r_{ij})$ is interaction energy of two particles at the distance r_{ij}

In that case we may use relation (28) to obtain mean value:

$$\langle U_N(\mathbf{r}^N) \rangle = \frac{1}{2} \int \int u(r_{ij}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (51)$$

Let's consider we have an isotropic case. Then pair distribution function depends only on distance, not on coordinates by itself:

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^{(2)}(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) \quad (52)$$

In that case we may rewrite (51)

$$\langle U_N(\mathbf{r}^N) \rangle = \frac{1}{2} \int u(r_{12}) \rho^{(2)}(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) \left(\int d\mathbf{r}_2 \right) d(\mathbf{r}_2 - \mathbf{r}_1) = \frac{V}{2} \int u(r_{12}) \rho^{(2)}(\mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1) \quad (53)$$

Using expression (17) we find:

$$\langle U_N(\mathbf{r}^N) \rangle = 2V\pi\rho^2 \int_0^\infty u(r_{12}) g(r_{12}) r^2 dr_{12} \quad (54)$$

Combaining together (48),(49),(54) we obtain final formula for the internal energy:

$$E = N \left(\frac{3}{2} k_B T + 2\pi\rho \int_0^\infty u(r) g(r) r^2 dr \right) \quad (55)$$

3 Partial molar volume

The partial molar volume is change in volume of NVT system due to adding one mole of particles to it. If the system consist of diferend particle species, each of them has its own partial molar volume. However, here we consider the case all particles are identical, and define partial molar volume:

$$v = \left(\frac{\partial V}{\partial N} \right)_{V,T} \quad (56)$$

I didn't find the exact formula to find partial molar volume. However, if we may rewrite (56) as:

$$v = \frac{\partial V}{\partial \mathcal{F}} = \frac{\partial \mathcal{F}}{\partial N} \quad (57)$$

where \mathcal{F} is *Helmholtz Free Energy*, defined in the previous chapter.

As well, we know how to find pressure P and chemical potential μ given Helmholtz Free Energy:

We may obtain chemical potential by derivating Free Energy over number of particles N :

$$\mu = \frac{\partial \mathcal{F}}{\partial N} \quad (58)$$

Pressure can be found by the formula:

$$P = -\frac{\partial \mathcal{F}}{\partial V} \quad (59)$$

Putting it to (57) we find:

$$v = -\frac{\mu}{P} \quad (60)$$

We already have equation for pressure (47). The only problem left to find chemical potential (58).

3.1 Chemical potential

As it is seen from relation (58), chemical potential is the change in Helmholtz Free Energy due to adding one more particle. That change might be found almost directly: We consider the case of pairwise potential. In that case the potential energy of system of N particles is:

$$U_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N u(r_{ij}) \quad (61)$$

The energy of system of $N+1$ particle is:

$$U_N(\mathbf{r}^{N+1}) = \sum_{i=1}^{N+1} \sum_{j=i+1}^{N+1} u(r_{ij}) = U_N(\mathbf{r}^N) + \sum_{i=1}^N u(r_{i,N+1}) \quad (62)$$

We may define a function

$$U_N(\mathbf{r}^N) = U_N(\mathbf{r}^N) + \lambda \sum_{i=1}^N u(r_{i,N+1}) \quad (63)$$

Where $0 < \lambda < 1$ is a coupling parameter, which "turns on" the potential of particle $(N+1)$.

In that case chemical potential might be found using *Thermodynamical Integration*:

$$\mu = k_B T \ln(\rho \Lambda^3) + 4\pi \rho \int_0^1 d\lambda \int_0^\infty u(r) g(r; \lambda) r^2 dr \quad (64)$$

Putting equations for chemical potential (64) and pressure (47) to the relation (60) we found:

$$v = -\frac{k_B T \ln(\rho \Lambda^3) + 4\pi \rho \int_0^1 d\lambda \int_0^\infty u(r) g(r; \lambda) r^2 dr}{\rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{\partial u(r)}{\partial r} r^3 g(r) dr} \quad (65)$$